



Feature Article

Successive synthesis of well-defined multiarmed miktoarm star polymers by iterative methodology using living anionic polymerization [☆]

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ARTICLE INFO

Article history:

Received 18 April 2013

Accepted 19 May 2013

Available online 4 June 2013

Keywords:

Miktoarm star polymer
 Multiarmed μ -star polymer
 Living anionic polymerization
 Iterative methodology
 Linking reaction

ABSTRACT

The synthesis of miktoarm star (μ -star) polymers by the methodologies based on living anionic polymerization is reviewed, with a particular focus on precisely controlled architectures of the synthesized μ -star polymers, such as molecular weight, molecular weight distribution, arm number, and composition. Among these methodologies, a novel and versatile stepwise “iterative methodology” recently developed by us is mainly introduced in this article. The iterative methodology is designed in a way that the same reaction site is regenerated after the arm introduction in each reaction sequence and this sequence is repeatable. The development of this methodology allows successive and, in principle, limitless introduction of arm segment into μ -star polymers. Consequently, a variety of new and synthetically very difficult multi-armed and multi-component μ -star polymers with well-defined architectures have been synthesized. They were composed of polyisoprene, poly(styrene)s, poly(2-vinylpyridine), poly(methyl methacrylate), various methacrylate-based polymers, and even poly(acetylene) as arm segments.

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1. Introduction

Star-branched polymers have been widely studied for a long time because of synthetic challenges associated with preparing them and because these polymers offer different properties and behavior from those of corresponding linear polymers. Among them, asymmetric star-branched polymers composed of chemically different arm segments, the so-called mixed arm or miktoarm (from the Greek word *μικτός* meaning mixed) star polymers, abbreviated as μ -star polymers, have received much attention in recent years. The addition of star-branched architectures to multiphase structures tremendously increases the variety of morphological suprastructures and molecular assemblies produced in bulk as well as in selected solvents, which are new, unique, and more importantly, quite different from those produced by linear block polymers [1–11]. Such nanoscale ordered materials may possibly play an important role in fabricating nano devices with many potential applications in the fields of nanoscience and nanotechnology. Thus, μ -star polymers are greatly expected to be promising multiphase polymeric materials next to block polymers.

In order to synthesize well-defined μ -star polymers which are necessary to elucidate morphological behavior, the use of living polymerization systems is essential. For such synthetic purposes, living anionic polymerization is the most preferred system in comparison with other living/controlled polymerization systems from the following viewpoints [12–15]: First, molecular weights can be precisely controlled in a wide range from 10^3 to even 10^6 g/mol. Second, extremely narrow molecular weight distributions are realized, M_w/M_n values being 1.05 or even smaller. Finally, living chain-end anions are highly reactive, but stable under appropriate conditions. In particular, the final viewpoint is important for the synthesis of multiarmed μ -star polymers, in which many linking reactions to introduce arm segments are required. For such reasons, we herein focus on the precise synthesis of multiarmed μ -star polymers by means of living anionic polymerization system.

As is known, it is far more difficult to synthesize μ -star polymers than regular stars having identical arms because the synthesis always requires selective multistep reactions that correspond to the number of different arms to be introduced, and isolation of intermediate polymers is often needed to obtain pure products. The developed methodologies so far based on living anionic polymerization can cover the synthesis of a two-component A_xB_y type and several 3-arm ABC μ -star polymers, but synthetic variation of μ -star polymers with more arms and components is quite limited [16,17].

The synthetic difficulty was undoubtedly attributed to the fact that there was no methodology, which allows for continued synthesis of μ -star polymers to further introduce arm segments because the reaction site(s) always disappear

after the introduction of arm segments. In order to overcome this difficulty, we have been developing a general and versatile methodology since 2001, which is based on a new conceptual “iterative approach”. In this methodology, the reaction system is designed in such a way that the same reaction site is always regenerated after the introduction of an arm segment in each reaction sequence, and this “arm introduction and regeneration of the same reaction site” sequence is repeatable. If this system well works, arm segments can be successively and, in principle, limitlessly introduced by repeating the reaction sequence to afford a series of multiarmed μ -star polymers.

In this article, we would like to introduce a quite novel methodology based on the “iterative approach” so far developed by us and show the effectiveness, versatility, and generality of the methodology in terms of the synthesis of multiarmed μ -star polymers with well-defined structures [18–24]. Since the living anionic polymerization system is herein used throughout the synthesis of such μ -star polymers because of the above-mentioned advantages, descriptions of μ -star polymers recently synthesized by living/controlled radical polymerization and other living polymerization systems are beyond the scope of this article and have been covered elsewhere.

2. General methodologies developed for the synthesis of μ -star polymers

Hadjichristidis and his coworkers reported an effective synthetic methodology for various μ -star polymers by exquisitely utilizing the different reactivity of a living anionic polymer toward each silyl chloride reaction site in multifunctional chlorosilane compounds. Scheme 1 shows the first successful synthesis of a 3-arm ABC μ -star polymer composed of polystyrene (PS), polyisoprene (PI), and poly(1,3-butadiene) (PB) arms [25]. The reactivity of living anionic polymers used for such arm segments appears to be in the order of the charge localization on the terminal carbon and in the opposite order of the steric hindrance, i.e., poly(1,3-butadienyl)lithium (PBLi) > poly(isoprenyl)lithium (PILi) > poly(styryl)lithium (PSLi). The synthesis was started by reacting PILi with a large excess of MeSiCl₃ to prepare a chain-end-SiCl₂-functionalized PI. After evaporation of excess MeSiCl₃, the resulting polymer was reacted with the least reactive PSLi in a titration manner, resulting in the formation of an in-chain-SiCl-functionalized PI-*b*-PS. Finally, the objective ABC μ -star polymer was obtained by the reaction of this silyl chloride-functionalized block copolymer with the most reactive PBLi. Similarly, a 4-arm ABCD μ -star polymer was synthesized by the same methodology with four different living anionic polymers in the following sequential addition order: PSLi, poly(4-methylstyryl)lithium, PILi, followed by PBLi [26]. Furthermore, various μ -star polymers

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